

Large Magnetovolume Effect in Yttrium Doped La-Ca-Mn-O Perovskite

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ac initial magnetic susceptibility, thermal expansion, and magnetostriction measurements were performed on a polycrystal of $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ manganese oxide. We observed a spontaneous volume magnetic contribution ($\cong 1 \times 10^{-3}$ at $T_C = 160 \pm 5$ K). This extra contribution sharply decreases at T_C as a consequence of the metal (M)-insulator (I) transition, and is suppressed under an applied magnetic field. This shows that the transition to the M state is induced by the field in the I regime, producing strong magnetoelastic effects. The present results demonstrate the close relationship between magnetoelastic and magnetotransport properties in this compound.

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The giant magnetoresistance (GMR) effect is being intensively investigated due to its scientific interest and also for the potential application of this phenomenon in magnetic recording technology. The "spin valve" effect observed in artificial metallic multilayers or superlattices [1,2] opened up a vast field of research. Increasing interest has recently also been focused on natural multilayered systems such as SmMn_2Ge_2 [3] where GMR of 4%–8% at low temperatures was observed and also on FeRh alloy which presents a GMR of 50% at room temperature [4]. Nowadays the rates of magnetoresistance have been considerably increased in thin films of perovskites $\text{La}_{1-x}\text{X}_x\text{MnO}_3$ ($X \equiv \text{Ba, Sr, Ca}$). These systems were extensively studied a long time ago [5–9]. The most attractive feature of their magnetic behavior was the existence of metallic conductivity and ferromagnetism. The magnetic interaction is well accepted as being the result of double exchange mechanisms [5] which require the presence of mixed valence Mn ions (Mn^{3+} and Mn^{4+}) as a consequence of the holes created by the replacement of La^{3+} by X^{2+} . Near the transition temperature T_C a large increase in the resistivity was observed in thin films of $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ [10], $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ [11], $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [12,13], and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [14]. The GMR has also been observed in bulk poly- and single-crystalline materials of $\text{Nd}_{0.5}\text{Pb}_{0.5}\text{MnO}_3$ [15] and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [16]. The resistivity data at temperatures above the magnetic transition were related to conduction by magnetic polarons [10,11,15]. The GMR effect has been observed in a polycrystal of $\text{La}_{0.67}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ [17], where $\Delta R/R \cong -10\,000\%$ near the magnetic ordering temperature T_C . Recently, Hwang *et al.* [18] considered that at T_C a ferromagnetic-metal (FMM) to paramagnetic insulator (PMI) transition takes place. Millis *et al.* [19] from theoretical considerations suggested a very strong electron-phonon coupling in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Tomioka *et al.* [20] in $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and Maritomo *et al.* [21] in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_3$ found evidence for the formation of a charge-ordered lattice (Wigner crystal) below a determined temperature. In this Letter we report

the discovery of a new magnetoelastic effect above T_C in $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ which is related to the nature of the carriers which drive the relevant magnetotransport properties in these perovskite compounds.

The $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ sample was prepared by using a gel precursor in order to obtain well-mixed reagents. Stoichiometric amounts of La_2O_3 , Y_2O_3 , CaCO_3 , and MnCO_3 with nominal purities higher than 99.9% were dissolved in concentrated nitric acid resulting in a light yellow solution. Afterwards, citric acid and ethylene glycol were added in a ratio of 4 g citric acid to 1 ml ethylene glycol and 1 g metal nitrates. The solution was heated and the excess nitric acid and water were boiled off giving a yellow-brown gel. The gel was heated to give a brown powder. This precursor was calcined in air at 1173 K overnight. The remaining black powder was cold pressed to 4 kbar and sintered at 1273 K for three days with intermediate grindings. Finally, the pellet was sintered at 1573 K for 8 h resulting in a hard black ceramic material. The sample was analyzed by means of x-ray powder diffraction resulting in a single phase with a perovskite-like structure.

Step-scanned powder diffraction patterns for $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ were collected at two temperatures ($T = 300$ and 100 K) using a D -max Rigaku system with rotating anode and a cryostat from Oxford Instruments. The diffractometer was operated at 45 kV and 160 mA and the $\text{Cu } K\alpha$ radiation was selected using a graphite monochromator. The temperature control was better than 0.1 K. Data were collected from 19° up to 140° in 2θ with a step size of 0.02° and a counting time of 8 and 5 s/step for the 300 and 100 K measurements, respectively.

Thermal expansion measurements were performed in two different ranges of temperature. Between 4 K and room temperature the strain gauge technique was used. In the high temperature range a "push rod" and differential transformer method was used. The magnetostriction measurements were carried out using the strain gauge technique under high pulsed field up to 14.2 T with a pulse

width of 50 ms and also under steady magnetic field up to 12 T. The ac initial magnetic susceptibility measurements were obtained using a mutual inductance method with an excitation field in the primary of 30 mOe and 20 Hz. Measurements of ac initial magnetic susceptibility were performed in the temperature range 5–300 K. The results are displayed in Fig. 1 where a very sharp increase in the ac magnetic susceptibility is observed at $T_C = (160 \pm 5)$ K. This anomaly is associated with the establishment of ferromagnetic order for temperatures below T_C . This temperature closely agrees with the sharp decrease in the electrical resistivity observed in this compound [17], which has also been tested in our sample.

Thermal expansion measurements suggest the existence of three different regions as can be clearly seen in Fig. 2. The temperature T_P is defined as the temperature at which an extra contribution appears over the phonon thermal expansion contribution $(\Delta l/l)_{ph}$. At temperatures where $T > T_P$ the linear thermal expansion is governed by the anharmonic phonon contribution. Within the temperature range $T_C < T < T_P$ the phonon contribution was calculated by using the Grüneisen law and a constant Debye temperature $\Theta_D = 500$ K. The theoretical prediction closely fitted the experimental results obtained from the thermal expansion measurements on a sample of LaMnO_3 . The extra contribution $(\Delta l/l)_P = \Delta l/l - (\Delta l/l)_{ph}$ is displayed in the inset of Fig. 2. At T_C a sharp decrease in the thermal expansion is observed with a volume lattice shrinkage of $\Delta V/V = 0.1\%$ ($\Delta V/V = 3\Delta l/l$). Asamitsu *et al.* [22] reported a structural transition below room temperature from rhombohedral to orthorhombic at low temperatures in the mixed valence perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. This was found to take place in a very narrow concentration range ($0.150 < x < 0.175$). In our case and following the Goldschmidt tolerance factor, the replacement of La^{3+} (ionic radius $r = 1.016$ Å) by Ca^{2+} ($r = 0.99$ Å) or Y^{3+} ($r = 0.893$ Å) instead of Sr^{2+} ($r = 1.12$ Å) leads to the stabilization of the orthorhombic structure at higher temperatures. So no

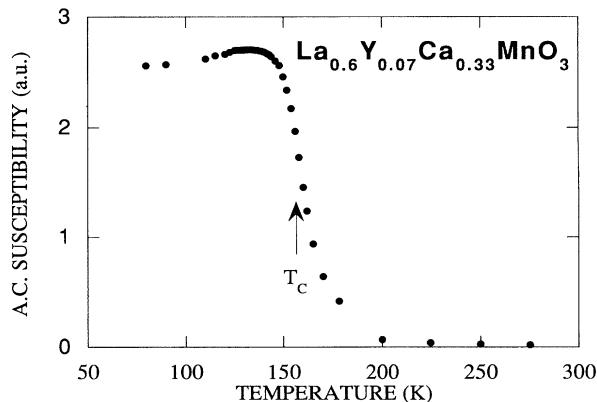


FIG. 1. Thermal dependence of the ac initial magnetic susceptibility of $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$.

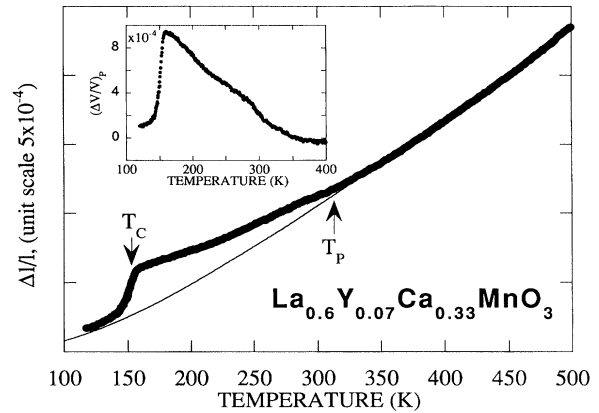


FIG. 2. Linear thermal expansion of $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$. Inset: anomalous thermal expansion contribution $(\Delta l/l)_P$.

changes in the crystal structure can be expected in the temperature range where the anomalous thermal expansion is detected. In order to test if this volume effect is related to a spontaneous change in the crystallographic structure at the magnetic transition we performed a careful x-ray analysis of the structure above and below T_C . The structure was refined using the program FULPROFF and a pseudo-Voigt function was used as the diffraction peak shape function. The sample has a slight orthorhombic distortion in the unit cell at both temperatures, showing a $Pbnm$ spatial group in agreement with the structure of related compounds [22]. Figure 3 shows, as example, the fitted diffraction pattern for $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ sample at 300 K. The final refined unit cells and atomic parameters are listed in Table I.

Parallel (λ_{\parallel}) and perpendicular (λ_{\perp}) magnetostriction to the applied magnetic field measurements at selected temperatures were performed in the temperature range 5–300 K. The obtained results showed a completely isotropic

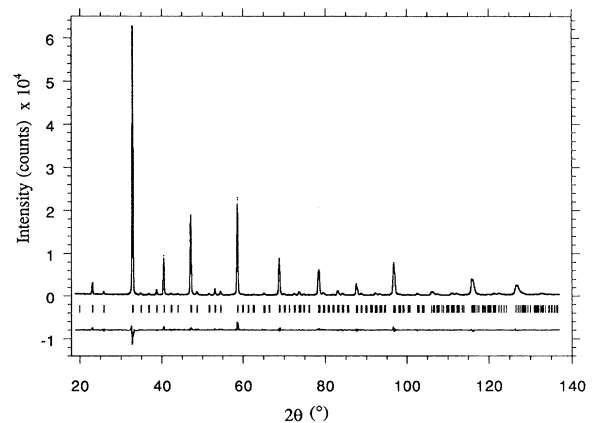


FIG. 3. X-ray diffractogram of $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ at 300 K. The line is a fit using the Rietveld method and parameters given in Table I. The difference is plotted at the bottom of the figure. The bars denote the calculated Bragg reflection positions.

TABLE I. Refined fractional atomic positions, average Debye-Waller factors (B_{av}), unit cell parameters, and conventional Rietveld unweighted (R_p), weighted (R_{wp}), and Bragg reliability factors (R_B). Standard errors in parentheses refer to the least significant digit. The atoms are located at the following Wyckoff positions. La (Y and Ca) at the 4(c): ($x, y, \frac{1}{4}$); Mn in 4(b): ($\frac{1}{2} 0 0$); O(1) in 4(c): ($x, y, \frac{1}{4}$); and O(2) at the 8(d): (x, y, z).

$\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$		100 K	300 K
Space group: <i>Pbnm</i>			
La/Y/Ca (0.6/0.07/0.33)	<i>x</i>	0.9975(6)	0.9978(6)
	<i>y</i>	0.0202(1)	0.0194(1)
	<i>z</i>	0.0705(33)	0.0768(17)
O(1)	<i>x</i>	0.4845(18)	0.4904(9)
	<i>y</i>	0.7341(22)	0.7239(14)
	<i>z</i>	0.2801(19)	0.2777(13)
O(2)	<i>x</i>	0.0377(13)	0.0316(8)
	<i>y</i>	0.17(1)	0.38(1)
	<i>z</i>	0.4845(18)	0.4904(9)
B_{av}		0.17(1)	0.38(1)
a (Å)		5.4392(3)	5.4551(2)
b (Å)		5.4498(2)	5.4552(2)
c (Å)		7.7144(4)	7.6966(1)
R_p		9.8	9.2
R_{wp}		12.6	10.4
R_B		6.2	5.8

behavior ($\lambda_{\parallel} = \lambda_{\perp}$) within the temperature range $T_C < T < T_P$. We have observed a small anisotropic contribution ($\lambda_t = \lambda_{\parallel} - \lambda_{\perp}$) below T_C as can be seen in Fig. 4. The inset of Fig. 4 shows a typical low anisotropic ferromagnet behavior below T_C with a small saturation anisotropic magnetostriction. In this temperature range the volume magnetostriction ($\omega = \lambda_{\parallel} + 2\lambda_{\perp}$) is also very small. In Fig. 5 the volume magnetostriction isotherms at selected temperatures are shown. As T_C is approached the negative volume magnetostriction sharply increases. The 170 K isotherm shows a tendency to a saturation value of $\omega = -1.0 \times 10^{-3}$ at 5 T. This volume magnetostriction is negative and has an absolute value similar to the spontaneous volume magnetostriction $(\Delta V/V)_p$. The thermal dependence of the anisotropic and volume magnetostriction at the maximum available field is shown in Fig. 6. A comparison of this magnetostriction results with the spontaneous anomalous contribution to the thermal expansion (see inset in Fig. 2) clearly shows that the mechanism which produces the spontaneous effect is suppressed by the application of a magnetic field. In order to test this effect we performed an experiment in which the thermal expansion was measured under a steady applied magnetic field up to 12 T. The results are shown in Fig. 7 where at fields greater than 5 T the anomalous contribution $(\Delta l/l)_{ph}$ is observed to be practically suppressed. In fact, the 12 T curve practically coincides with the calculated Gruneisen curve (see Fig. 2).

The present thermal expansion and magnetostriction results on the Y doped La-Ca-Mn-O compound in connection with the magnetotransport properties indicate a strong electron-phonon and spin coupling. Because the anoma-

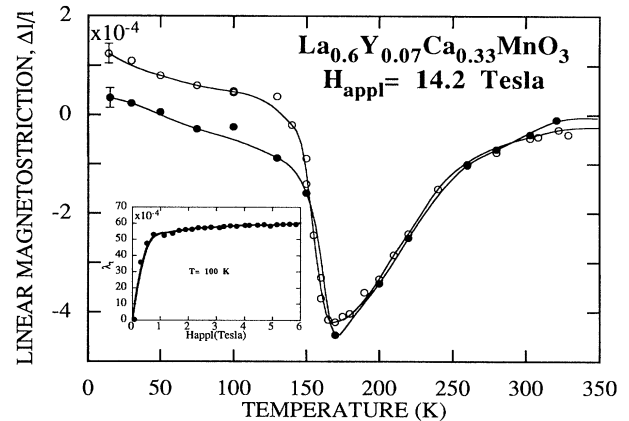


FIG. 4. Thermal dependence of the parallel (○) and perpendicular (●) magnetostriction at the maximum applied field of 14.2 T. Inset: Anisotropic magnetostriction isotherm at 100 K.

lous contribution to the thermal expansion takes place well above T_C , we consider that this contribution is originated by a carrier localization process (polaron effect) as has recently been observed in other related compounds [20,21]. This localization is gradual and produces a local distortion [23] as temperature decreases. This distortion starts as T_P , the temperature at which the linear thermal expansion deviates from the phonon anharmonic contribution represented by the Grüneisen curve (see Fig. 2). This mechanism may be responsible for the insulator state (PMI). At T_C the establishment of the long range ferromagnetic order through the double exchange interaction brings the system below T_C into a metallic state (FMM). The sharp decrease of $\Delta l/l$ at T_C can be explained as the consequence of the charge delocalization. This lattice shrinkage brings the lattice parameter to a value which practically corresponds to the phonon lattice expansion. Below T_C the sole additional contribution to the phonon thermal expansion is produced by the spatial dependence

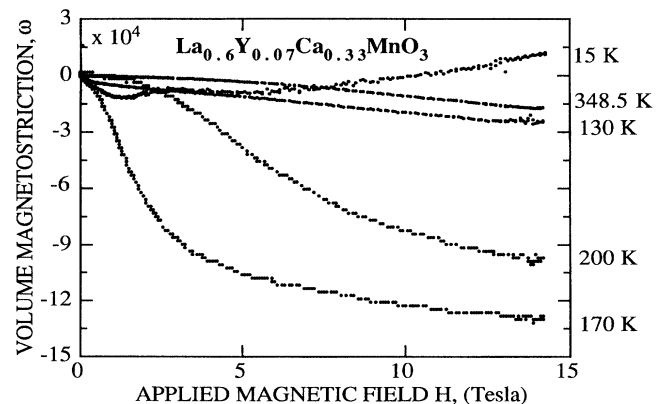


FIG. 5. Volume magnetostriction isotherms of $\text{La}_{0.6}\text{Y}_{0.07}\text{Ca}_{0.33}\text{MnO}_3$ at selected temperatures.

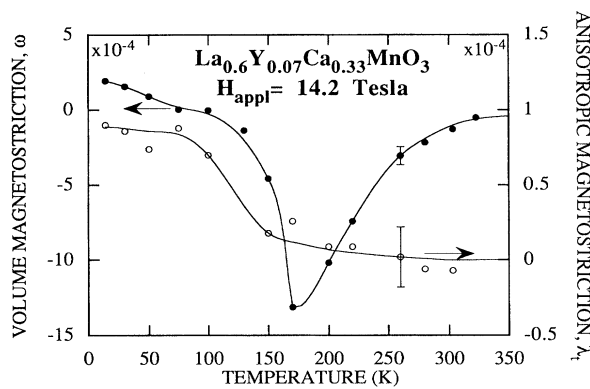


FIG. 6. Thermal dependence of the volume and anisotropic magnetostriction at the maximum field.

of the exchange interaction. This contribution is small and irrelevant in the present study.

The magnetostriction measurements clearly suggest two different mechanisms above and below T_C . In the paramagnetic phase $T_C < T < T_p$ the measure magnetostriction is isotropic ($\lambda_{\parallel} = \lambda_{\perp}$) and gives rise to a volume distortion of the same magnitude as the spontaneous distortion originated by charge localization but of contrary sign. This would indicate that the localization mechanism is quenched under the application of a determined magnetic field. This field effect on localized charges has recently been observed in a generalized charge ordered lattice [20]. The magnetostriction in the FM phase is anisotropic and typical in value and shape to a ferromagnetic $3d$ metal, the volume magnetostriction being negligible.

In summary, two different mechanisms have been found for the magnetostriction above and below T_C which can be explained, in the same way as the magnetotransport properties in related compounds [19,20], as a crossover through T_C from a FMM low-volume (low temperature ground state) toward a charge localized PMI high-volume (ground state above T_C). Both of these states are almost degenerate in energy and can be reached either by thermal activation or by applied magnetic field. The observed magnetoelastic effect produced by charge-lattice

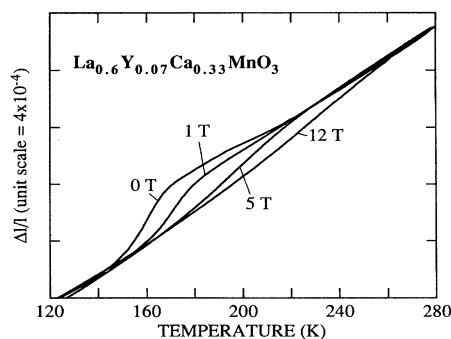


FIG. 7. Thermal expansion measurements under several applied magnetic fields.

and spin-lattice coupling should be considered as relevant information in order to clarify the origin of the magnetotransport properties in this and related manganese perovskite oxides. These magnetostrictive effects could also be interesting from the point of view of the application of this and other related materials (presently under study) as magnetostrictive transducers. However, it should be considered as a limitation in applications of these compounds as GMR materials.

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